Optical and mechanical properties of alumina films fabricated on Kapton polymer by plasma immersion ion implantation and deposition using different biases

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Received 14 May 2007; accepted 8 June 2007
Available online 15 June 2007

Abstract

Alumina films are fabricated on Kapton polymer by aluminum plasma immersion ion implantation and deposition in an oxidizing ambient and the effects of the bias voltage on the film properties are investigated. Rutherford backscattering spectrometry (RBS) reveals successful deposition of alumina films on the polymer surface and that the O to Al ratio is higher than that of stoichiometric Al₂O₃. The thickness of the modified layers decreases from 200 to 120 nm when the bias voltage is increased from 5 to 20 kV. Our results indicate that higher bombardment energy may lead to higher crack resistance and better film adhesion. However, a higher sample bias degrades the optical properties of the films as indicated by the higher absorbance and lower energy band gap. Therefore, the processing voltage must be optimized to yield a protective layer with the appropriate thickness, superior optical properties, as well as high crack resistance.

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PACS: 52.77.Dq; 61.82.Pv

Keywords: Plasma immersion ion implantation and deposition; Alumina films; Rutherford backscattering spectrometry; Optical properties; Crack resistance

1. Introduction

The external surfaces of spacecrafts are usually protected by a thermal blanket to control the surface temperature. However, damage of polymeric materials by atomic-oxygen (AO) in the low-earth-orbit (LEO) can adversely affect the performance of this thermal blanket [1,2]. It has been reported that the interaction of AO with polymers results in surface erosion, changes in chemical composition and surface morphology, altered optical properties, and formation of particulate and molecular contamination on the spacecraft surface [3,4]. Hence, enhancement of the oxidation and erosion resistance of polymeric surfaces is important in order to ensure that the coefficients of solar absorptance and thermal emittance of thermal blanket is only slightly changed or even unchanged during its lifetime [5–7]. Ceramic materials such as Al₂O₃ have been proven to be good protective coatings. However, the fragile nature of Al₂O₃ films has hitherto limited its applications in spacecrafts. Aluminum ion implantation followed by oxidation has been reported to create an elastic barrier layer to protect polymers against erosion by AO [8], but if the layer is too thin, it is not durable. In addition, AO may diffuse through the protective coating into the coating/polymer interface causing damage if the protective coating is too thin [1].

Plasma immersion ion implantation and deposition (PIII&D) is an effective surface modification technique boasting advantages such as non-line-of-sight operation and combined energetic ion implantation and low-temperature plasma deposition [9]. This technique has been applied to polymers to improve the mechanical properties [10], electrical conductivity [11], anti-erosion by oxidation [12], and antibacterial performance [13–15]. In this work, aluminum was plasma-implanted and deposited by means of a cathodic
vacuum arc into Kapton foils to produce an alumina coating and the effects of the bias voltages on film properties are investigated.

2. Experimental details

A filtered vacuum arc was utilized to produce aluminum ions to fabricate aluminum oxide films on Kapton polymer foils (100 μm in thickness). The polymer samples were positioned 15 cm away from the exit of the curved magnetic filter duct. Spring steel clips covered with aluminum foil were used to fix the Kapton foils onto the aluminum stage to reduce the risk of electrical arcing during PIII&D. The Kapton foil was first immersed in a hydrogen plasma produced by radio frequency (RF, 13.56 MHz) with the power of 200 W and gas pressure of $1.4 \times 10^{-4}$ Torr for 10 min. Active functional groups may be created so that the adsorbing power of the polymeric surface can be enhanced [16,17]. Afterwards, aluminum PIII&D was performed in the presence of oxygen at a flow rate of 10 sccm and working pressure of $2.4 \times 10^{-4}$ Torr. The samples were biased to a DC voltage of $-500$ V as well as pulsed voltages of $-5$, $-10$, and $-20$ kV, respectively. In pulsed PIII&D, the pulse duration was 150 μs whereas the aluminum arc plasma pulses had a duration of 300 μs. This led to a hybrid process consisting of both ion implantation and deposition. The total PIII&D time was 60 min.

Rutherford backscattering spectrometry (RBS) offers the better means of providing both the composition and elemental depth profiles for the nanometer-thick foils [18]. It was performed using 2 MeV $^4$He$^{++}$ and a backscattered angle of 170°. The exact composition of the films was essential to the proper interpretation of the absorption spectra obtained. The transmission spectra of the foils were obtained using an ultraviolet-visible spectrophotometer (Perkin Elmer, Lambda 2s). The pin scratch test and mechanical folding test were employed to evaluate the crack behavior of the alumina coatings.

3. Results and discussion

The RBS spectra of the alumina films on Kapton are depicted in Fig. 1. The SIMNRA code [19] was used to fit these spectra assuming the same chemical composition in the four layers. The solid line in Fig. 1 denotes the simulated spectrum calculated by the SIMNRA code for each alumina film. The aluminum signal and oxygen peak in the simulated spectra fit the experimental data very well. The aluminum signals detected at a backscattered energy of around 1100 keV and oxygen signals at around 700 keV indicate the formation of alumina films on the Kapton foils. The aluminum signals beneath the top surface of the high-bias (several 10 kV) samples can be attributed to high energy ion implantation and recoil implantation of deposited aluminum. When the bias voltage is higher (e.g., $-20$ kV), more aluminum ions are injected into the polymer (see the inserted drawing). Thus, the films are expected to possess better adhesion on the foils. It is noticed that the film thickness is different for different biases as shown in Fig. 2. The thickness of the modified layer decreases from 200 to 120 nm with the bias increasing from $-5$ to $-20$ kV possibly due to sputtering effects.

![RBS Spectra](image_url)
The RBS data are further analyzed to estimate the relative concentration of aluminum and oxygen and the results are shown in Fig. 3. The retained aluminum dose is up to $10^{17}$ atoms/cm$^2$ on the surface. The relative atomic ratio of oxygen to aluminum varies from 1.4 to 2.1 indicating nonstoichiometric Al$_2$O$_3$. This extra oxygen may be incorporated as O–H and C–O groups in the coatings [20,21]. It is also observed that the ratio of oxygen to aluminum changes substantially when the bias changes from $-10$ to $-20$ kV. It is perhaps due to different preferential sputtering effects of oxygen and aluminum at $-20$ kV.

The optical properties are measured using a Perkin-Elmer Lambda 2s UV/VIS spectrophotometer with wavelength ranging from the near-infrared to ultraviolet. As shown in Fig. 4(a), the untreated Kapton foil shows nearly full transmission in the near-infrared and visible region as well as total absorption in the UV region. With increasing negative bias, the transmittance decreases as shown in Fig. 4(b). At a wavelength of 800 nm, the transmittances are 80.46%, 73.03%, 64.39% and 60.06% for the untreated substrate and foils plasma-implanted at $-5$, $-10$ and $-20$ kV, respectively. In fact, the optical properties from ultraviolet to near visible are totally changed when the bias is $-20$ kV [inset in Fig. 4(b)]. Generally, the higher the ion bombardment energy, the lower is the transmittance even for the thinner layer deposited at a higher bias ($-20$ kV), although it has been reported that alumina films have high transparency down to 250 nm [22]. High energy ion bombardment may produce better adhesion on the foils due to mechanical interlocking [23] and chemical bonding [24]. However, the degree of carbon–carbon bond breaking and substrate degradation may be more severe leading to the higher absorbance as shown in Fig. 5. Therefore, a proper bias must be chosen to yield both good adhesion and optical properties.

The absorption coefficient $\alpha$ of alumina film on Kapton can be calculated from the obtained absorbance and thickness data. Furthermore, the absorption coefficient $\alpha$ can be applied in the Tauc extrapolation plot to determine the optical band gap. The optical band gap $E_g$ calculated on the basis of the Tauc relationship is [25]:

$$ (\alpha E)^{1/2} = B(E - E_g), $$  

where $E$ is the phonon energy and $B$ is the Tauc slope. The intensity of the UV light passing through the polymer substrate and alumina film can be written as:

$$ I_1 = I_0 e^{-\alpha t}, $$

where $I_0$ is the light intensity of original UV, $I_1$ is the light intensity of the UV after passing the samples, and $t$ is the alumina film thickness determined by RBS. The absorbance $A$
of the sample is defined as:

\[ A = \ln \left( \frac{I_0}{I_1} \right) = -\ln T, \quad (3) \]

where \( T \) is the transmittance of the sample being equal to \( I_1/I_0 \). From Eq. (2) and (3), the absorption coefficient can be obtained by:

\[ \alpha = \frac{A}{t}. \quad (4) \]

The photon energy \( E \) (eV) is described by the equation:

\[ E = \frac{(hc)}{e\lambda}, \quad (5) \]

where \( h \) is Planck constant, \( c \) is the speed of light, \( e \) is the electron charge, and \( \lambda \) is the wavelength. The direct optical band gaps can then be calculated by extrapolation of the curve on the basis of the Tauc plot of \((\alpha E)^{1/2} \) versus the photon energy \( E \) as illustrated in Fig. 6. The intersection of the linear extrapolation of these curves along the \( x \)-axis may give an indirect band gap [26]. Our results demonstrate that the band gaps range from 2.071 to 2.140 eV depending on the biases. The optical band gap decreases with increasing sample bias. The optical band gap is determined by the degree of damage in the Kapton polymer and alumina layer. Therefore, when ion bombardment is severe, a smaller band gap results.

The crack resistance is very important for protective films since undercutting can easily proliferate when the film is damaged [27]. Fig. 7 shows the typical fracture surface on the treated samples after scratching with a pin. There are many hackles along the scratch track, and small hackles follow the main hackles due to impact loading. The crack paths are zigzag like at the boundary of the scratch track. Different biases produce different crack behavior. Brittle fracture is observed for a smaller bias, for example, −5 kV. Most of the cracks terminate at the coating–substrate interface [28] due to plastic deformation in the relatively ductile substrate [29]. In contrast, when the bias is higher (e.g., −10 kV), there are no hackles along the scratch track although some cracks are also observed due to larger plastic deformation in the substrate.

The crack resistance to mechanical folding is of practical importance for the AO-resistant films as they are frequently wrapped in applications associated with spacecrafts. A mechanical folding test is performed to assess the crack behavior of the alumina films on Kapton. Fig. 8 illustrates schematically the folding test in which the specimens of the same size are used. The cracks may initiate due to the folding-induced stress and the cracks spread perpendicularly to the folding direction as shown in Fig. 9. In the sample treated at −5 kV, several micro-cracks parallel to the folding direction are also observed. This may be related to releases stress waves [30]. The alumina film flakes off on the local surfaces after the
folding test, although it is frequently cohesive as shown in Fig. 9(a). The sample treated at $-10$ kV possesses similar surface cracks as shown in Fig. 9(b). However, flaking is not found with the exception of micro-cracks demonstrating better adhesion. Surprisingly, micro-cracks in the alumina film fabricated at $-20$ kV can hardly be observed in Fig. 9(c). These results suggest that a higher processing voltage is beneficial to the reduction of crack initiation and propagation. The crack resistance of the AO-resistant films is one of critical factors determining the AO erosion rate.

The adhesion mechanism can be separated into mechanical interlocking, physical bonding, and chemical bonding [31]. In all the substrate/coating systems, these mechanisms are responsible for the adhesion, either singly or in concert. During the hybrid plasma deposition and implantation process, mechanical interlocking plays a dominant role due to high energy ion bombardment, and the formation of ionic bonding in the aluminum oxide seems possible under certain conditions [32]. A micro-crack serves to relax the stress at the crack tip and enlarge the amount of area that supports the loading. The residual strength of the damaged zone is the key factor governing the main crack initiation especially in thicker brittle films [33]. A higher ion bombardment energy may enhance the adhesion and deformational strength, but the optical transmittance of Kapton polymer may be adversely affected. Hence, a proper bombardment energy is needed to fabricate the protective films with better adhesion and optical properties.

4. Conclusion

Alumina films produced on Kapton polymer with enhanced AO resistance capability are fabricated by plasma immersion ion implantation and deposition. With increasing bias voltages, the thickness of deposited films decreases due to sputtering. The alumina coatings are oxygen rich as determined by RBS. A higher sample bias induce more extensive ion mixing and recoil implantation to achieve better adhesion and higher crack resistance. However, a higher bombardment energy may degrade the optical properties. Consequently, the bias voltage must be optimized in order to fabricate protective alumina films with both good mechanical and optical properties.

Acknowledgments

The work was jointly supported by Natural Science Foundation of China (No. 10575025 and No. 50373007), Program for New Century Excellent Talents in University in
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